

PHYSICAL PROPERTIES OF THE LIQUID OZONE-FLUORINE SYSTEM*

Charles K. Hersh and A. J. Gaynor

IIT Research Institute
Chicago, Illinois

INTRODUCTION

The utilization of ozone and fluorine as liquid oxidizers has been an aim of rocket technologists for many years. It has been known for some time that liquid ozone and fluorine are miscible over the entire composition range, in contrast to the ozone-oxygen system, which has a consolute temperature of 93°K.

Investigators at NASA have computed the specific impulse of ozone-fluorine mixtures with JP-4 and have shown that a maximum occurs at about 30 wt % ozone.¹ The physical properties necessary for a more complete evaluation of this system have not been available. It was, therefore, the purpose of this study to measure the density, surface tension, viscosity, and vapor-liquid equilibria.

EXPERIMENTAL

Density

A borosilicate glass U-tube, 4 mm in I.D. and 10 cm long, was used for the density measurements.² A measured amount of liquid ozone was transferred to the U-tube, and the procedure was repeated with enough liquid fluorine to result in a solution of the desired concentration. The valves separating the legs of the U-tube were closed and the solution was mixed. The metal tubes containing the equilibrium vapor over each leg were then heated slightly. Since the vapor consisted almost entirely of fluorine, it is believed that heating did not change the composition, but caused the gas to bubble through the liquid, thus insuring thorough mixing. While a slight pressure was maintained on one leg of the U-tube, the liquid level of the ozone-fluorine mixture and the level of the reference fluorocarbon manometer were measured with a cathetometer. The densities obtained in this manner are shown in Table 1.

These data were then reduced to straight line functions on the Institute's Univac 1105 computer by the method of least squares. The computer program for this purpose was available from a previous study, hence the reduction was readily accomplished. Equations for determining the density of liquid ozone-fluorine mixtures at the two temperatures investigated are:

$$\rho_{-183^{\circ}\text{C}} = 0.1009 (\text{wt fraction } \text{O}_3) + 1.4704 \quad (1)$$

(deviation = ± 0.0013)

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$$P_{-195.8^{\circ}\text{C}} = 0.0534 (\text{wt fraction } \text{O}_3) + 1.5611 \quad (2)$$

(deviation = ± 0.0024)

Table 1

DENSITY OF LIQUID OZONE-FLUORINE MIXTURES

Temperature, °C	Ozone Concentration, wt %	Density, g/cc	
		Measured	Calculated*
-183	0.0	1.472	1.470
	31.0	1.499	1.502
	84.6	1.557	1.556
	100.0	1.571	1.571
-195.8	0.0	1.561	1.561
	23.0	1.573	1.573
	61.8	1.595	1.594
	100.0	1.614	1.615

* From Eq (1) and (2).

Viscosity

The viscosity of ozone-fluorine mixtures was determined in a modified Ostwald viscometer,² which was used with a variable volume of liquid. The viscometer was made from precision-bore, glass tubing (4 mm in I.D.) with a capillary section 0.203 mm in diameter and 12 cm long.

To force the liquid to a convenient height above the capillary section, either helium pressure was used, or the metal tubes containing the equilibrium vapor over each leg were heated after the valves had been closed. Then the valve isolating the two arms of the viscometer was opened and the readings of the height, h , of liquid as it fell through the capillary were taken as a function of time. The driving pressure was proportional to the difference between the liquid and the equilibrium levels ($h - h_e$) and, in uniform bore tubing, the rate of flow was proportional to dh/dt . Hence, for liquids following Poiseuille's law, $\log(h - h_e)$ should be proportional to the time of flow. In every case a linear relation between $\log(h - h_e)$ and time was obtained, which shows that ozone-fluorine solutions are Newtonian fluids.

For convenience, the half time ($t_{1/2}$), which is the time required for the liquid to fall one half the distance from the initial level to the equilibrium level, was determined from graphs of the time-height functions. The viscosity was calculated from the equation:

$$\mu = Ct_{1/2}^2 \rho \quad (3)$$

where

- μ = viscosity
 ρ = density of the fluid, g/cc
 C = an apparatus constant determined with liquids of known viscosity (1.289×10^{-2} centipoise-cc/sec-gram).

The results shown in Table 2 represent at least two independent measurements for each viscosity reported.

Table 2

VISCOSITY OF OZONE-FLUORINE MIXTURES

Ozone Concentration, mole %	Viscosity, cp	
	-183°C	-195.8°C
100.0	1.55 \pm 0.01	4.15 \pm 0.04
79.1	0.905 \pm 0.01	
70.5		1.95 \pm 0.01
30.5	0.343 \pm 0.03	
26.8		0.682 \pm 0.02
0.0	0.208 \pm 0.01	0.344 \pm 0.01

Surface Tension

The surface tension of various ozone-fluorine mixtures was determined by the capillary rise method in the apparatus used for the viscosity measurements.² The following equation was used:

$$T = \frac{r h \rho g}{2} \quad (4)$$

where

- T = surface tension
 r = radius of capillary, cm
 h = capillary rise, cm
 ρ = density of solution, g/cc
 g = gravitational constant, cm/sec²

Results at -183 and -195.8°C are given in Table 3.

Table 3

SURFACE TENSION OF OZONE-FLUORINE MIXTURES

Ozone Concentration, mole %	Surface Tension, dynes/cm	
	-183°C	-195.8°C
100.0	39.9	43.5
79.1	30.2	
70.5		35.6
30.5	19.1	
26.8		22.4
0.0	12.3	15.5

Vapor Pressure

Two different techniques were used in determining the vapor pressure of various liquid ozone-fluorine mixtures, depending on the pressures to be measured. The first technique was developed for measurements at low pressures (to 1.5 atm). The liquid ozone, which was condensed at liquid oxygen temperature (-183°C) into a calibrated glass tube, was pumped on at reduced pressure to remove any residual oxygen, and then the total volume was measured with a cathetometer. The measured amount of ozone was then transferred quantitatively to a glass tube by distillation. The above procedure was repeated with liquid fluorine condensed at liquid nitrogen temperature (196°C), and the two liquids were allowed to come to equilibrium before a vapor pressure reading was taken. Readings were taken at bath temperatures of 75.7, 77.7, and 90.2°K. These temperatures were measured with an oxygen vapor pressure thermometer. After the initial values had been determined, additional known amounts of fluorine were admitted to the U-tube, and vapor pressure readings were again taken. The data obtained in this manner for a series of ozone-fluorine mixtures are given in Fig. 1.

Considerable time was required for the liquid mixtures to come to equilibrium in the original U-tube, and it was thought that a stirring bar would ensure a homogeneous solution of the two liquids in the modified apparatus. However, in each of the three attempts to use a Teflon-coated stirring bar on the 90 mole % ozone mixtures, the apparatus was destroyed by an explosion. Apparently, the mixtures which have high ozone concentrations are as sensitive to the wiping action of the stirring bar along the glass surface of the reservoir as is 100% ozone (from previous experience).

The values at greater than 50 mole % ozone were obtained in a reservoir which has a large cross-sectional area, in the hope that this apparatus would facilitate mass transfer between the two liquid phases (fluorine on top of ozone).

In the second technique (to 20 atm), the apparatus was an all-metal system similar to that used for measurements on ozone-

oxygen mixtures.³ The test chamber was constructed of stainless steel. It consisted of 1-inch bar stock (1-1/2 inches long), Swagelok fittings, a pressure gauge, and a copper-constantan thermocouple. The system had a volume of 20.1 cc.

The experimental procedure consisted of determining the liquid lines. The results are shown in Fig. 2. When the volume of vapor in a closed system is kept small relative to the volume of liquid, the amount of liquid that must be vaporized to give a 20-atm pressure is small. Thus, the composition of the liquid will be changed by only a negligible amount. For these determinations the composition of the charge was known accurately, and provision was made for agitation of the test bomb.

As determined by this method, the vapor pressure of pure fluorine was found to be in agreement with the value reported by Landau,⁴ and the vapor pressure of oxygen was found to be in agreement with the value reported in NBS Circular No. 564.⁵ This verified that fact that the pressure and temperature indicators were correct relative to each other.

RESULTS AND CONCLUSIONS

The density studies indicate that liquid ozone-fluorine mixtures are homogeneous and not subject to decomposition at the temperatures investigated. Some of the liquid mixtures detonated during this study, but only those of high (greater than 60 wt %) ozone concentration. This apparent hazard should not be disturbing, since calculations show that the theoretical specific impulse of systems containing JP-4 and ozone-fluorine mixtures is at a maximum when the oxidizer consists of 30 wt % ozone in fluorine. A mixture of this composition requires very few handling precautions over those observed with 100% liquid fluorine.

Liquid ozone is approximately ten times more viscous than fluorine at -183°C; but even liquid ozone supercooled at -195.8°C flows readily (4.15 cp). The viscosity of the solutions decreases rapidly as fluorine is added, and a semilog relation is approximated when viscosity is plotted as a function of composition at -183 and -195.8°C. The surface tension of ozone is approximately three times that of fluorine.

The vapor pressure studies were straightforward, and the results indicate nothing out of the ordinary when the vapor pressures of the individual components are compared with those observed for the mixtures. The importance of these tests, however, lies in the fact that they show the liquid ozone-fluorine mixtures to be homogeneous and not subject to decomposition at the temperatures investigated.

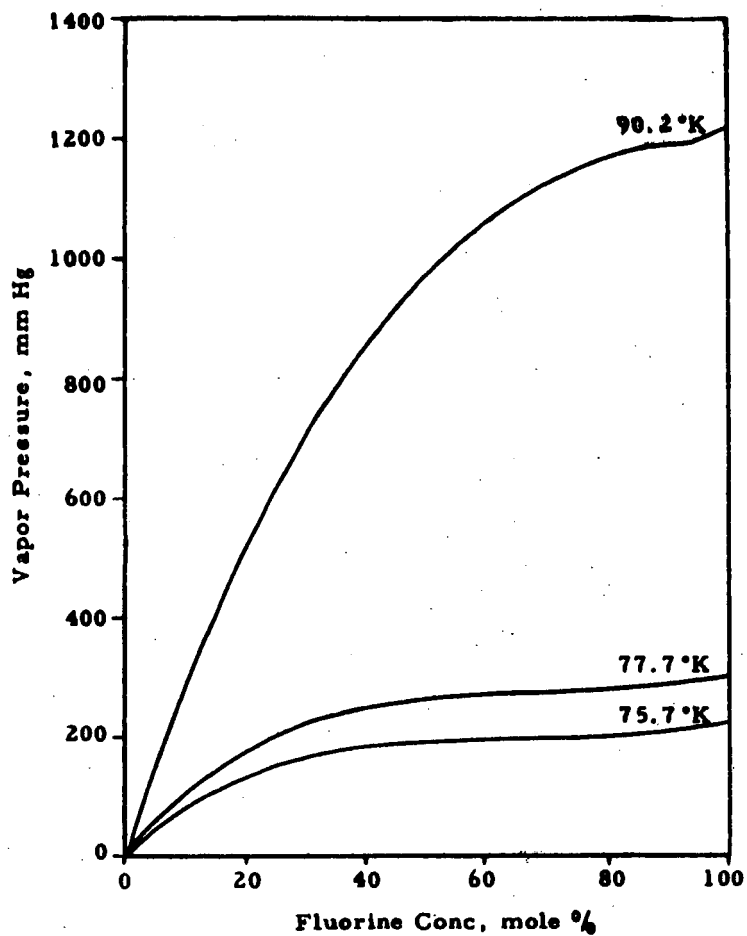


Figure 1
VAPOR PRESSURE OF LIQUID OZONE-FLUORINE MIXTURES

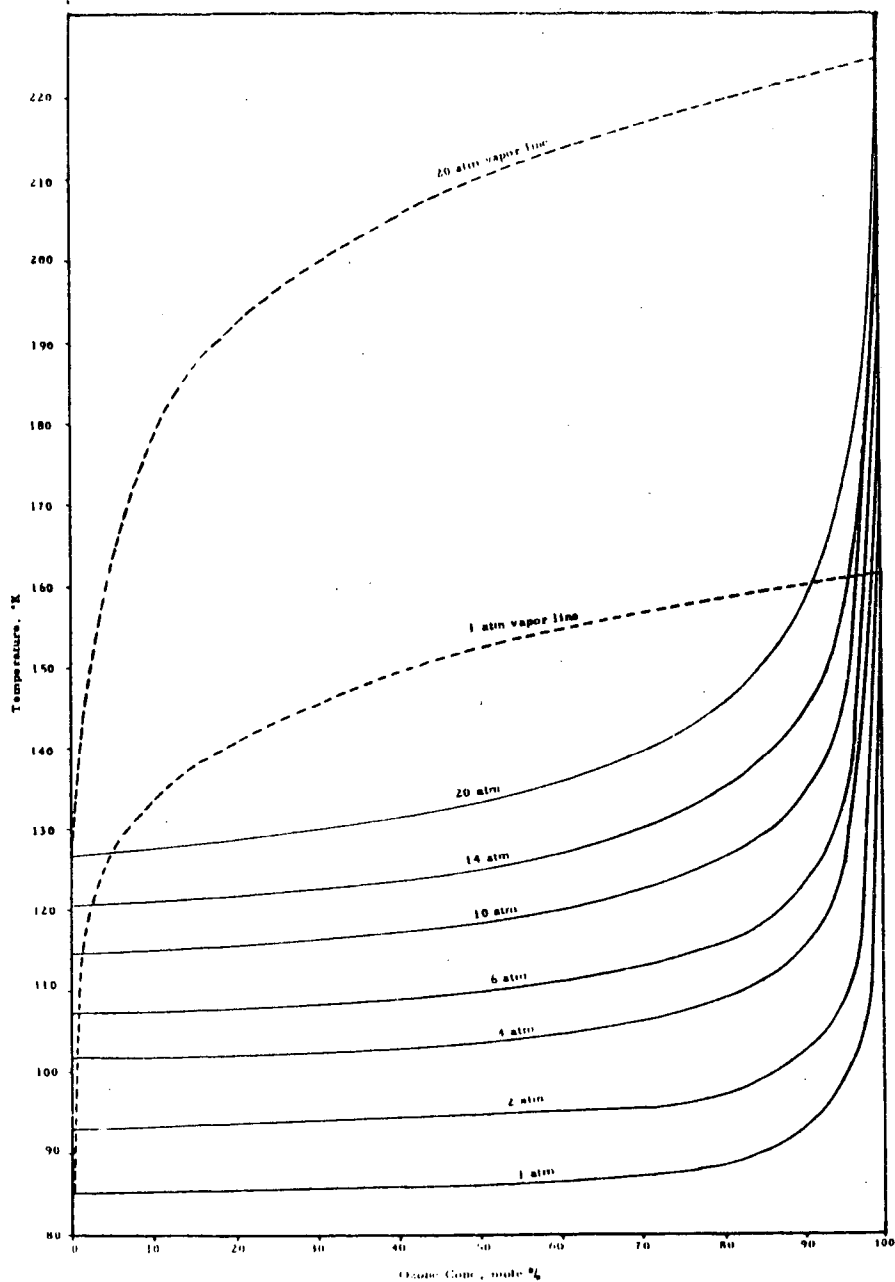


Figure 2

VAPOR-LIQUID EQUILIBRIUM DIAGRAM OF OZONE-FLUORINE SYSTEM

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